# Distribution control of protecting groups and its effect on LER for EUV molecular resist

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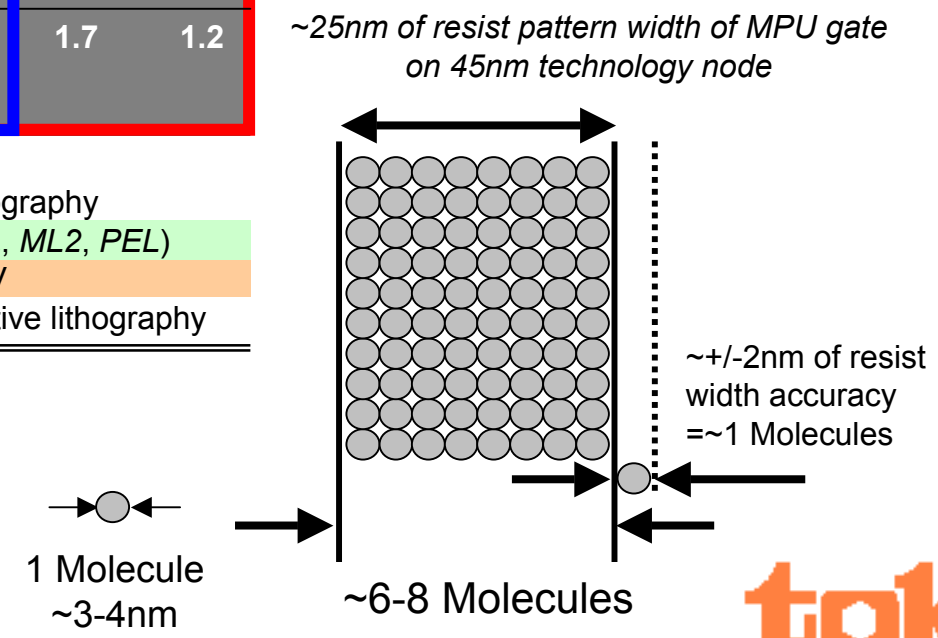
# *Key lithography-related characteristics and resist requirements on the ITRS 2005*

**Table** Key lithography-related characteristics and resist requirements on the ITRS 2005.

| Year of production | 2007 | 2010 | 2013 | 2016 |
|---|---|---|---|---|
| Technology Node | hp65 | hp45 | hp32 | hp22 |
| DRAM half pitch (nm) | 65 | 45 | 32 | 22 |
| MPU Gate in resist length (nm) | 42 | 30 | 21 | 15 |
| MPU Gate Length after etch (nm) | 25 | 18 | 13 | 9 |
| MPU Gate CD control (3sigma) (nm) | 2.6 | 1.9 | 1.3 | 0.9 |
| Line Width Roughness (LWR) (3sigma, <8% of CD) (nm) | 3.4 | 2.4 | 1.7 | 1.2 |
| Lithography Exposure Tool | 193nm + RET | 193nm immersion lithography | | |
| Potential Solutions | | EB (*EPL*, *ML2*, *PEL*)<br>EUV<br>Innovative lithography | | |

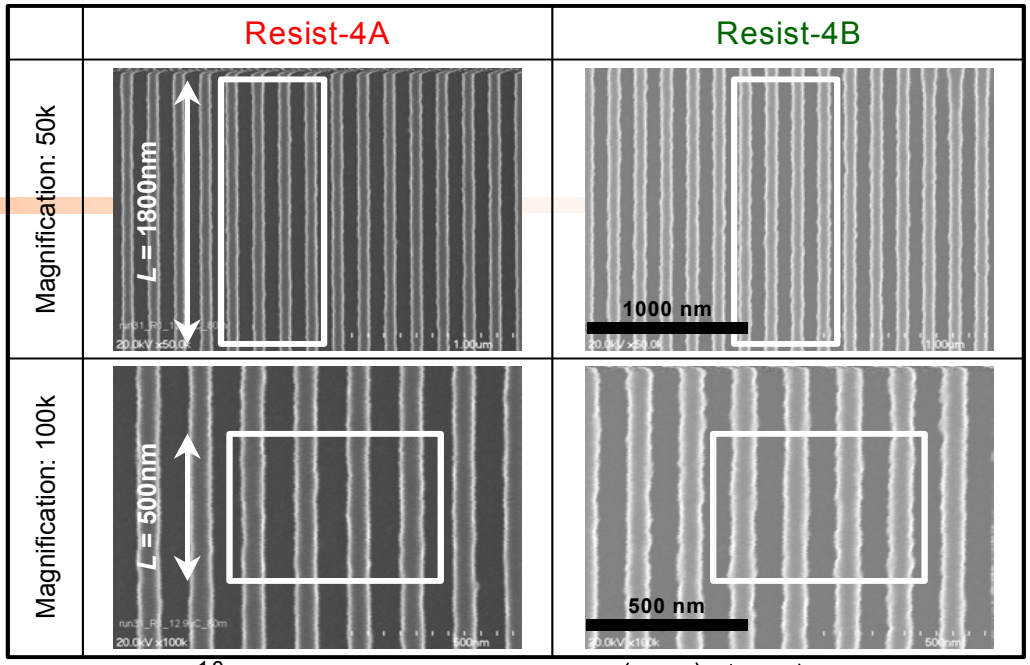
: Manufacturable solutions are NOT known

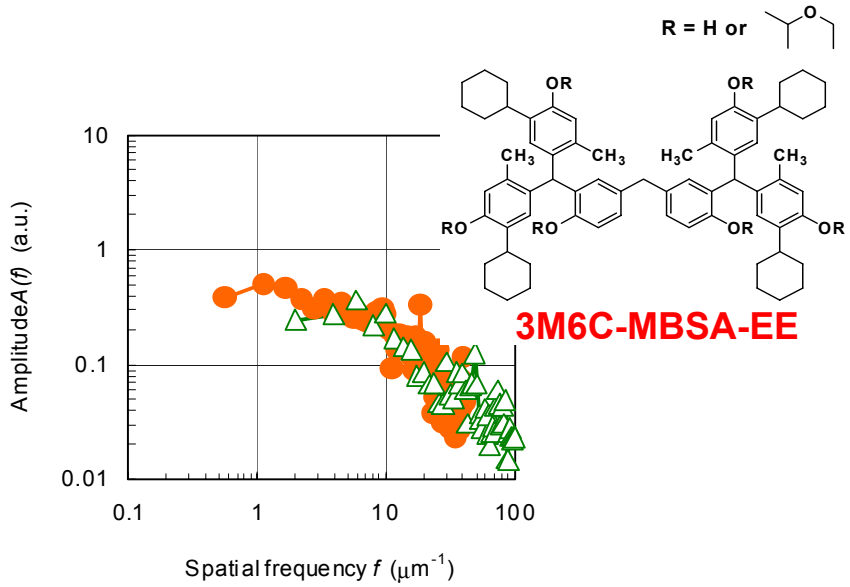
*RET: resolution enhancement technology*
*EB: electron beam lithography*
*EPL: electron projection lithography*
*ML2: maskless lithography*
*PEL: proximity electron lithography*
*EUV: extreme ultraviolet*

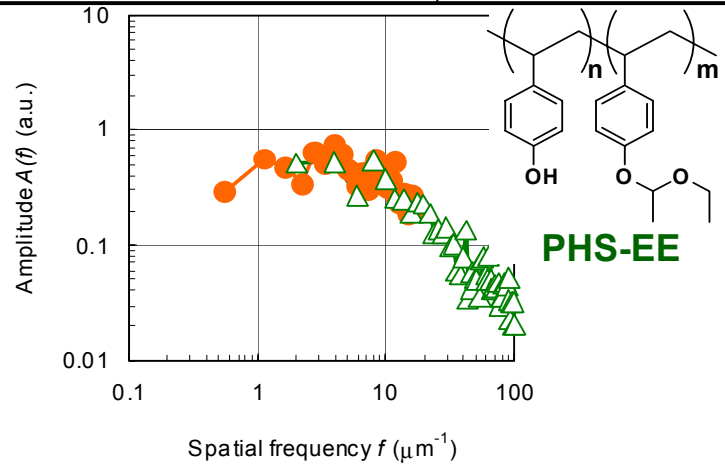


# Our Previous Work
# Molecular resist vs. Polymer

80nm L/S patterning tests with EB exposure and LER analysis of **Molecular Resist** (Resist-4A) were performed as compared with **polymeric resist** (Resist-4B).




**Molecular resist (Resist-4A)**
**LER (3sigma, *L*=1800nm) = 5.1 nm**

**Polymer resist (Resist-4B)**
**LER (3sigma, *L*=1800nm) = 7.4 nm**

**Figure** The Fourier amplitude spectra and the LER[2)] of resist-4A and 4B.


1) T. Hirayama et al.: *Polym. Adv. Technol.*, **17** (2006) 116-121.
2) A. Yamaguchi et al.:*J. Photopolym. Sci. Technol.*, **16** (2003) 387.

# *Our Previous Work; Further LER improvement concerning protecting group distribution*

## < HPLC analysis >

**Crude Platform**
(non to 4 parts protecting groups mixture)

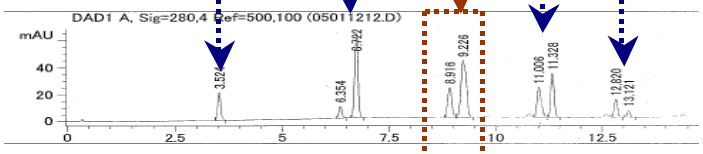
**2 parts protecting**

**1 part protecting**

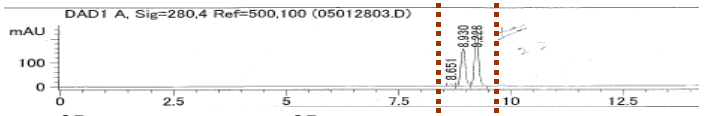
**4 parts protecting**

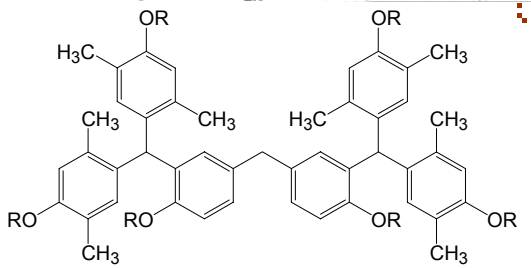
**3 parts protecting**

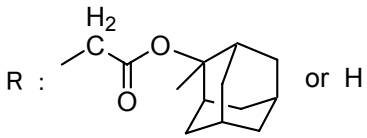
**Non protecting**




**Purifying Platform**
(only 2 parts protecting group)

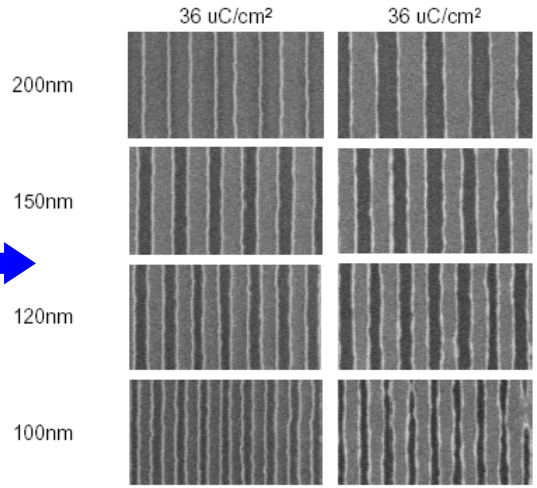



**Resolution, LER**
**Purifying Platform >>> Crude Platform**

**Purifying Platform** (only 2 parts protecting group) | **Crude Platform** (non to 4 parts protecting groups mixture)




***Controlling distribution of protecting groups have a great impact on improvement of LER***

3) T. Hirayama et al.: SPIE 6153-18 (2006)

## *Material design for improving LER*

- *Low molecular size*
- *No distribution of the protecting groups*
- *Chemically amplified positive-tone*
- *Thermal property for lithography process*
- *Etching durability*

# *Molecular size comparison*

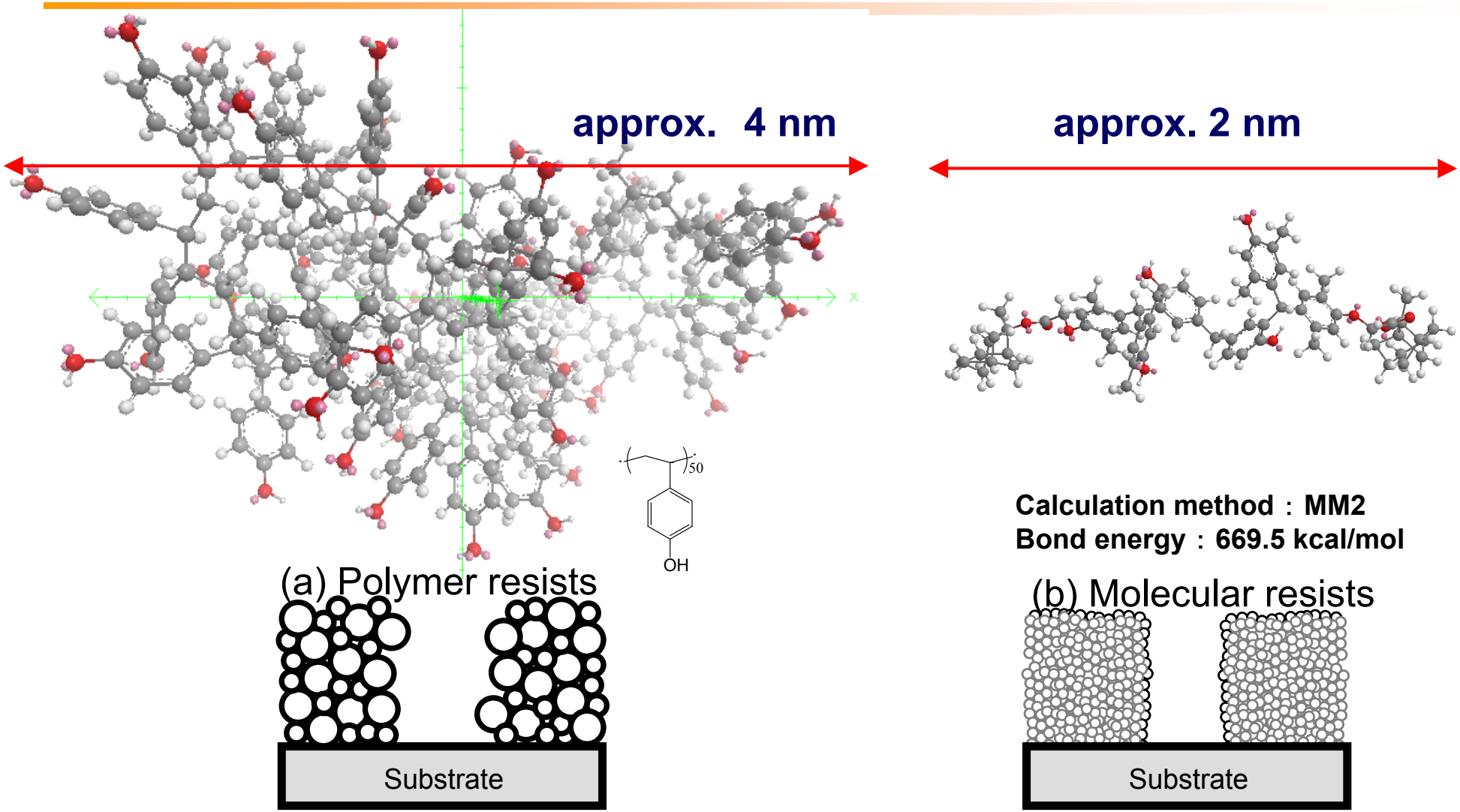
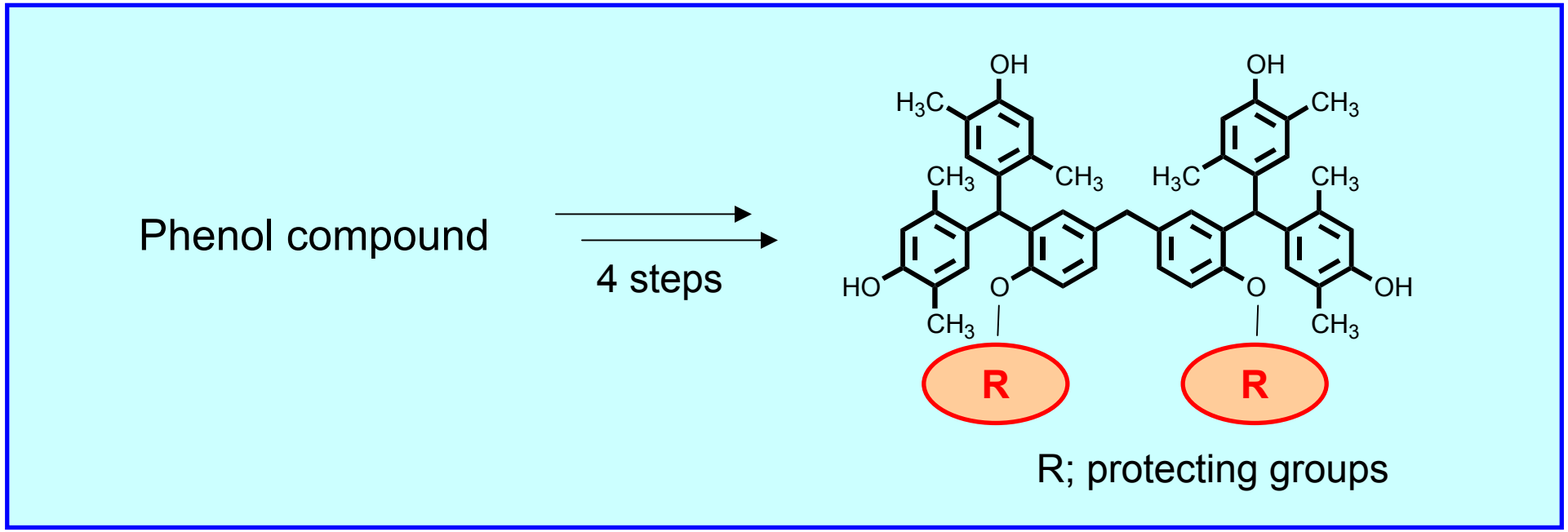



**Figure.** Schematic illustrations of cross sectional resist pattern based on (a) the conventional polymeric material and (b) the low molecular base matrix.

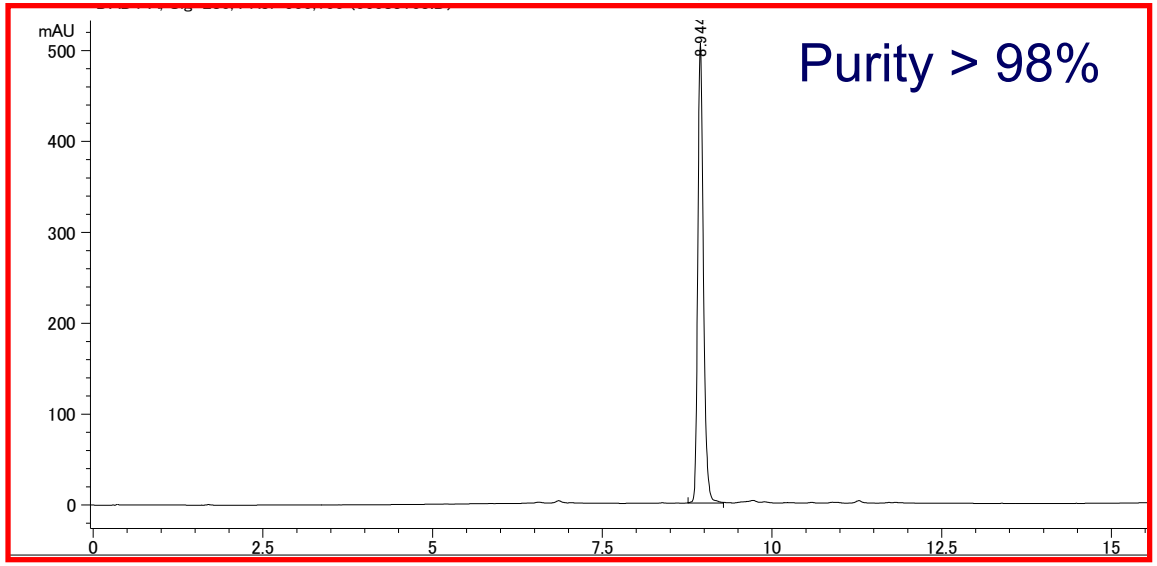
*T. Kadota, et.al., Proc. SPIE, 4345 (2001) 891.*

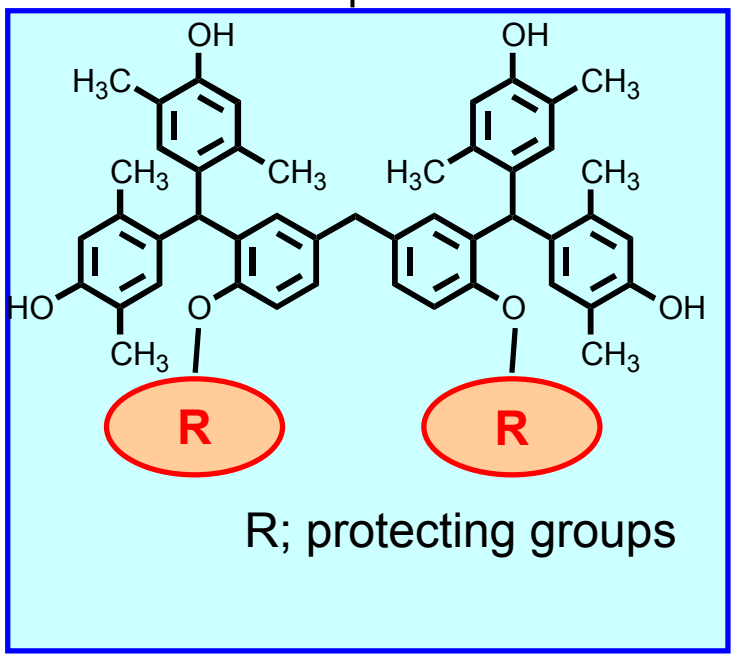
# *Synthesis of molecular resist*




***We have designed and synthesized a molecular resist material, which has no distribution of the protecting group.***

# *Purity analysis of molecular resist material*

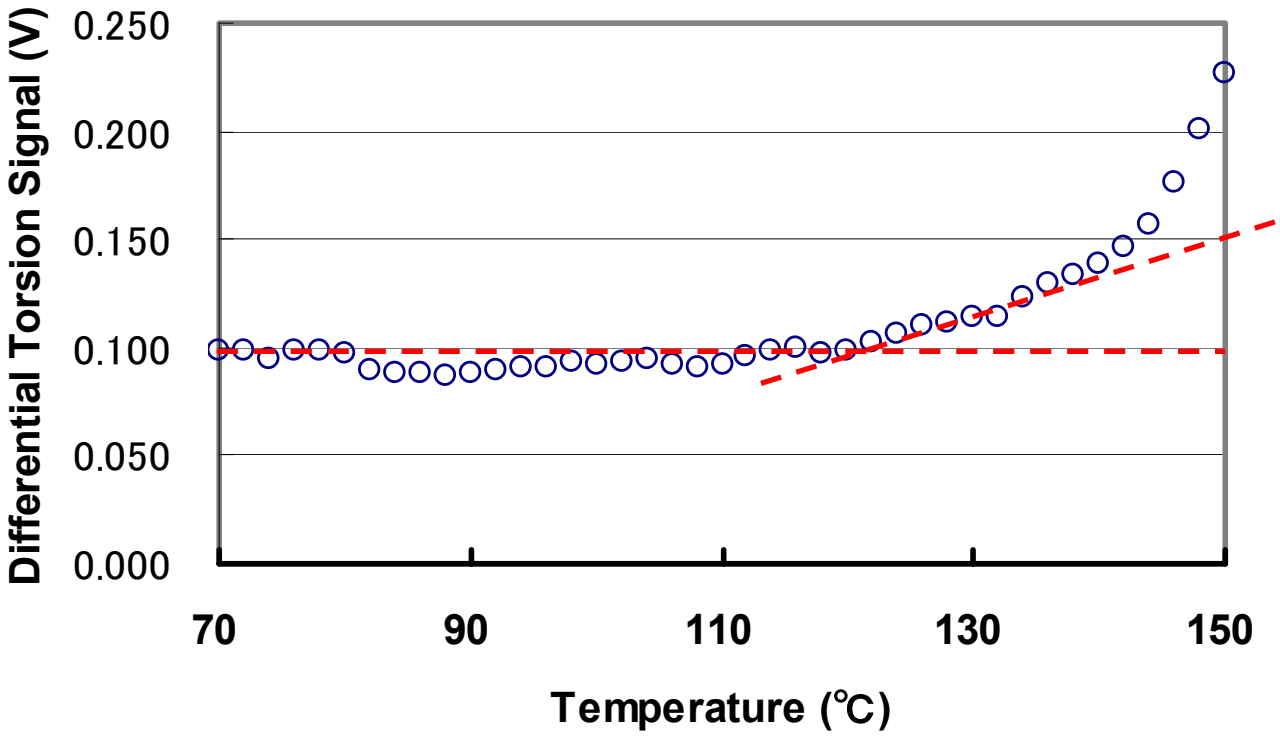


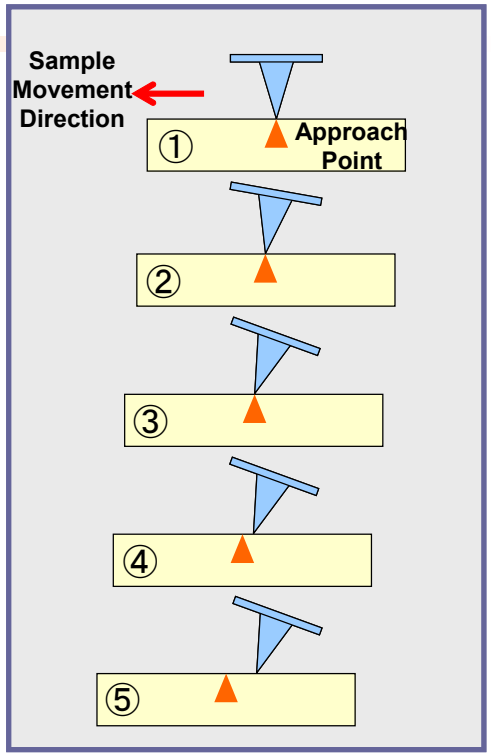



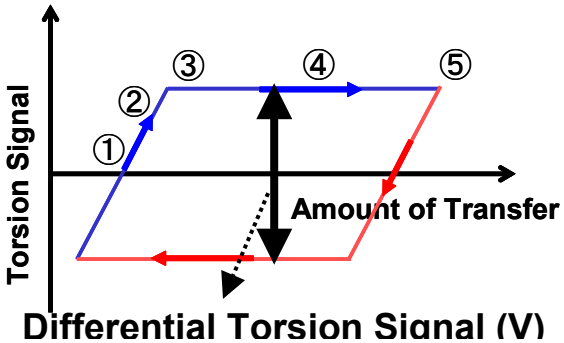

Hewlett Packard, Series 1100
Column Shiseido C-18 MG 3um 4.6*75mm
Inspection wave length; 280nm

# *Thermal property*

**The molecular resist surface has started to go soft around 120 °C**




*FFM :Frictional Force Microscopy
E-sweep (SII NanoTechnology Inc.)

* T. Kajiyama et al.: *Macromolecules.*, 27 (1994) 7932.

# Etching durability

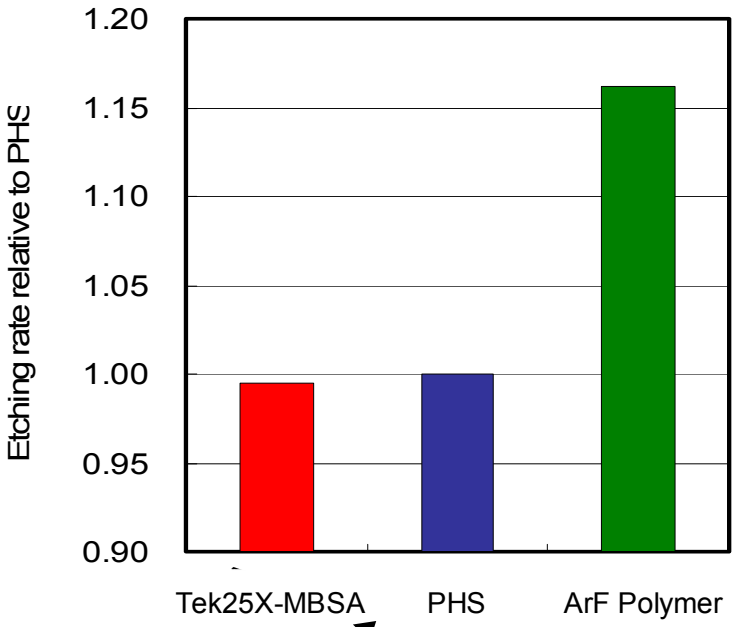
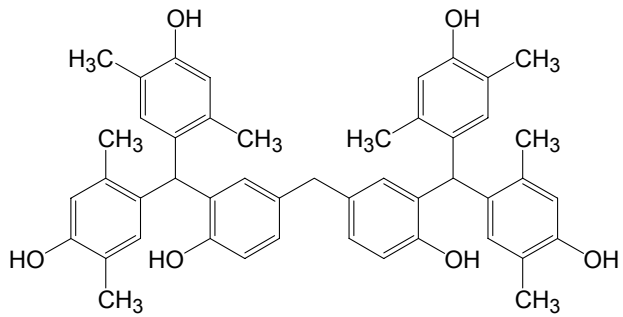



**Table** Ohnisi-parameter of several polymers.
*Carbon density parameter* = $N / (N_C - N_O)$,
where, $N$ is number of the total atoms, $N_C$ is Number of carbon atoms and $N_O$ is number of oxygen atoms

| 25X-MBSA | Novolak resin | PHS | ArF methacrylic polymer |
|---|---|---|---|
| 2.46 | 2.43 | 2.50 | 3.44 |




**Tek25X-MBSA**

4) T. Hirayama et al.: J. Photopolym. Sci. Technol., 17 (2004) 435.

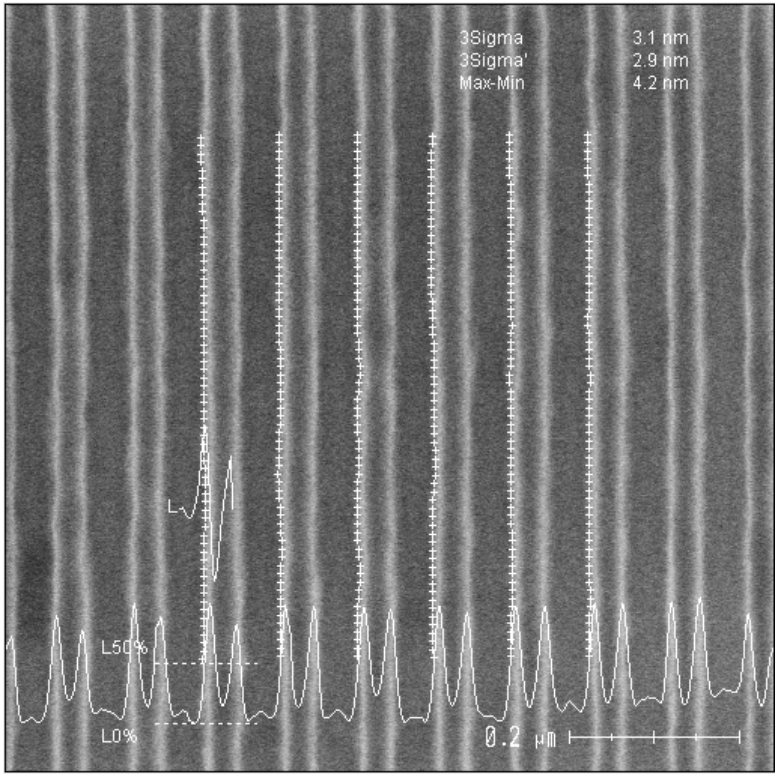
# *Design of High-NA Small-field Exposure Tool at ASET and Specifications of Pattern Replications*

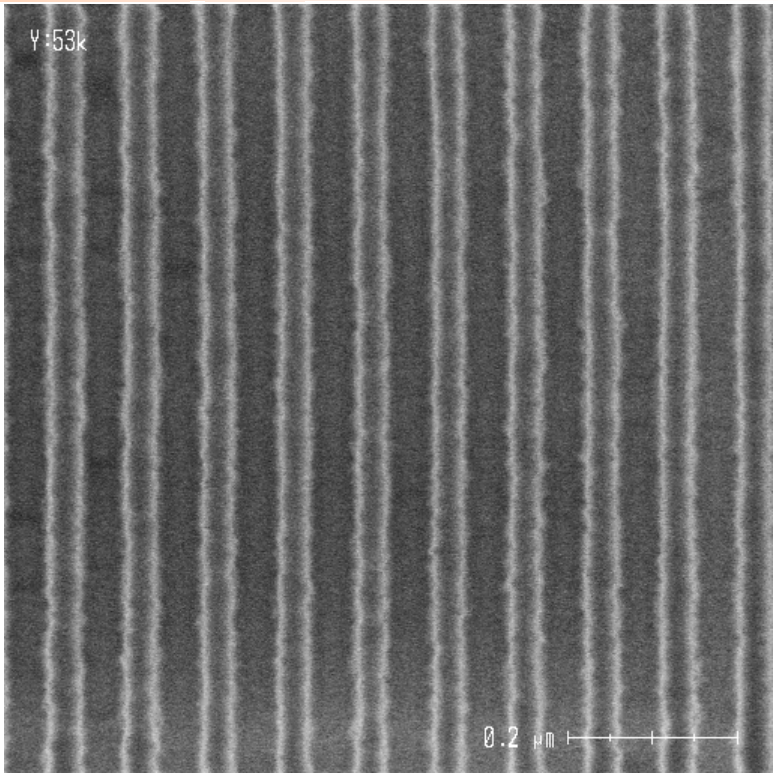
- Exposure wavelength: 13.5 nm (SR:bending magnet)
- Magnification: 1/5
- Two-aspherical-mirror projection optics
  - NA: 0.3
  - Field size: 500 x 300 μm
- Mask size: 6025 reticle
- Wafer size: 8"Φ

**WFE of the HINA3: 0.91 nm (λ/15)**

- Reflection Mask: Mo/Si d-spacing = 7 nm, 40 pairs
  - Absorber and buffer : 65~90-nm-thick TaGeN and 10-nm-thick Cr
  - Absorber and buffer : 90-nm-thick TaBN and 10-nm-thick CrX
- Evaluated Conditions
  - Resist System: CA positive-tone resist based on Tek25X-MBSA
  - Resist film Thickness: 100 nm)
  - Exposure: Illumination condition σ~0
  - PAB: 110 °C-90 s
  - PEB: 100 °C-90 s
  - Exposure Dose: 12.2 mJ/cm$^2$
  - Development: aqueous 0.26 N tetramethylammonium hydroxide (TMAH) at 23°C
  - SEM: S-9380 (Hitachi)

# *The result of molecular resist on EUV*




| | |
|---|---|
| **LER @ 45nm L/S = 3.1nm**<br>**inspection length; 620nm × 6 lines**<br>**(scan mode; normal-scan)** | **LER @ 45nm L/S = 3.6nm**<br>**inspection length; 2000nm × 6 lines**<br>**(scan mode; rectangular-scan)** |

# Summary

- ***We have synthesized a molecular resist material which is completely controlled structure with no distribution of the protecting groups***
- ***The molecular resist performance has shown as follows:***
  - ***Molecular resist material with no distribution of protecting group showed the glass transition temperature around 120℃.***
  - ***Uniform amorphous thin film***
  - ***LER Analysis (L=620nm) of 3.1nm @ 45nm L/S***
  - ***LER Analysis (L=2000nm) of 3.6nm @ 45nm L/S***

# *Acknowledgements*

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) under the management of the Key Technology Research Promotion Program